

**Title****Methods And Devices For Recycling Copper From A Discarded Circuit Board And A Discarded Fluid Containing Copper****Field of the present Invention**

The present invention relates generally to a process for recycling copper from a substance containing the copper, and more particularly to the methods and the devices by which the copper is completely recycled from a discarded printed circuit board (PCB) and from a discarded fluid containing the copper.

**Background of the present Invention**

As a result of the rapid development of information technology in recent years, the use of the low-end computers as well as the hand sets is wide-spread. Such a wide-spread use of the computers and the hand sets brings about a substantial increase in demand for the printed circuit board. Accordingly, the discarded printed circuit boards pose an environmental problem. In light of the fact that the process for making PCB involves the use of a chemical etching solution, such as copper chloride or the like. As a result, the process for making PCB results in production of a discarded fluid containing an extremely high concentration of copper ions. Without being properly treated, the discard fluid poses a potential environmental hazard. In addition, the copper which is contained in the discarded fluid should be recycled as a matter of cost-effectiveness. It is therefore imperative that copper should be recycled from a discarded or rejected PCB for economic and environmental reasons. A number of electronic components are attached to the PCB by tin soldering. The tin can be easily recycled by use of a stripping fluid. However, the copper contained in the discarded or rejected PCB can not be easily recycled by use of a stripping fluid. There are two conventional methods, by which the copper contained in the discarded PCB is recycled. These two conventional methods are described hereinafter.

The first conventional method involves the comminution of the discarded printed circuit boards. By virtue of the principle of specific gravity, the powder is divided into two groups, one of which contains a greater amount of copper. This

method is rather primitive and ineffective at best.

The second conventional method involves the burning of the glass fiber and the adhesive of the discarded printed circuit boards. The adhesive contains epoxy resin and bromide. As a result, the burning of the adhesive is bound to produce bromine hydride which is a pollutant. In addition, the burning of the glass fiber must be done at a temperature greater than 1000 degrees in Celsius and is therefore not cost-effective.

### Summary of the present Invention

The primary objective of the present invention is to provide an economically feasible method for recycling copper that is contained in the discarded printed circuit boards or the discarded fluid which is resulted from the electroplating process or the etching process of the PCB production. The method involves the saturation of copper ions, which are then reduced by use of sodium carbonate or sodium hydroxide.

Another objective of the present invention is to provide a copper recycling method, which involves use of hydrochloric acid. The discarded printed circuit boards are showered with the hydrochloric acid to obtain a fluid containing copper. The copper-containing fluid is provided with sodium carbonate, thereby resulting in formation of sodium salt and copper carbonate. The sodium salt can be crystallized by heating for industrial application. The copper carbonate is converted by heating into copper oxide, which is sold to generate an additional income. This method is economical and free from a pollutant.

Another objective of the present invention is to provide a method for recycling copper which is contained in the discarded printed circuit boards. The method involves the use of hydrochloric acid or sulphuric acid, by which the copper is ionized in a solution. The solution is then provided with sodium hydroxide to form sodium salt and copper hydroxide. The copper hydroxide is converted by heating into copper oxide, which can be used as an industrial material. Meanwhile, the sodium salt is crystallized by heating for industrial application.

Another objective of the present invention is to provide a copper recycling process in which the discarded printed circuit boards are bathed in a solution

containing oxalic acid ( $\text{HOOCCOOH} \cdot 1/2\text{H}_2\text{O}$ ). The copper contained in the discarded printed circuit boards is made into copper oxalate ( $\text{CuC}_2\text{O}_4 \cdot 1/2\text{H}_2\text{O}$ ), which is precipitated and harvested. The copper oxalate is heated in presence of oxygen so as to be converted into copper oxide which is of a commercial value.

A further objective of the present invention is to provide a process for recycling copper that is contained in the discarded printed circuit boards. The process involves the use of hydrochloric acid or sulphuric acid, in which the discarded printed circuit boards are bathed to produce a solution containing the copper ions. An aluminum material is then introduced into the solution to result in formation of copper powder. The aluminum-containing solution can be used as PAC in the water treatment. The aluminum is used in the process by virtue of the aluminum being greater in activity than the copper.

#### **Brief Description of the Drawings**

Fig.1 shows a flow block diagram of a first preferred embodiment of the present invention.

Fig.2 shows a flow block diagram of a second preferred embodiment of the present invention.

Fig.3 shows a flow diagram of a third preferred embodiment of the present invention.

Fig.4 shows a flow block diagram of a fourth preferred embodiment of the present invention.

Fig.5 shows a flow block diagram of a fifth preferred embodiment of the present invention.

Fig.6 shows a schematic view of a device which is used in the preferred embodiments as shown in Figs.1 through Fig.5.

Fig.7 shows a flow block diagram of a sixth preferred embodiment of the present invention.

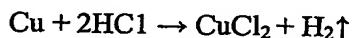
Fig.8 shows a flow block diagram of a seventh preferred embodiment of the present invention.

Fig.9 shows a schematic view of a device which is used in the preferred embodiments as shown in Fig.7 and Fig. 8.

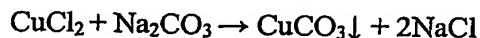
### Detailed Description of the Preferred Embodiments

It must be noted here that the present invention deals with the recycling of the copper that is contained in a discarded printed circuit board (PCB). Accordingly, the electronic components of the PCB and the tin solder, by which the electronic components are attached to the PCB, are not the subject matters of the present invention.

Referring to Fig.1, a method embodied in the present invention is used to recycle copper from the discarded printed circuit boards. The method involves a first step in which a predetermined number of the discarded printed circuit boards are immersed in the hydrochloric acid (HCl) so as to cause copper contained in the discarded printed circuit boards to remain in the ionizing state, thereby resulting in formation of a copper chloride ( $CuCl_2$ ) solution. The chemical reaction is expressed as follows:



Thereafter, the copper chloride ( $CuCl_2$ ) solution is mixed with a predetermined amount of sodium carbonate ( $Na_2CO_3$ ), as illustrated by the following chemical reaction:



The copper carbonate ( $CuCO_3$ ) is precipitated and harvested. The copper carbonate is converted by heating into copper oxide ( $CuO$ ), as shown in the following chemical reaction.

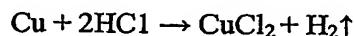


The copper oxide is used as an industrial raw material. The sodium chloride (NaCl) is also used as an industrial raw material. However, the sodium chloride so formed must be first crystallized by heating prior to being used as the industrial raw material.

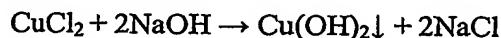
The use of the hydrochloric acid is to effect the ionization of the copper that is contained in the discarded printed circuit boards. The copper ionization can be enhanced by use of hydrogen peroxide, aeration, or electrode. The reduction of the copper ions is brought about by use of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).

It must be noted here that the hydrochloric acid may be replaced by an electroplating waste fluid, etching waste fluid, or copper chloride waste fluid, which is a waste product of the manufacturing process of PCB. These waste fluids contain copper, as well as ionizing acid capable of ionizing the copper. The copper ions are then reduced by sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), thereby resulting in formation of copper carbonate ( $\text{CuCO}_3$ ), which is then converted by heating into copper oxide ( $\text{CuO}$ ).

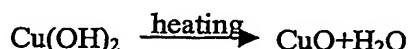
As shown in Fig.2, a second method embodied in the present invention is intended to recycle copper from the discarded printed circuit boards. This second method comprises an initial step in which the discarded printed circuit boards are immersed in the hydrochloric acid (HCl) so as to form a copper chloride ( $\text{CuCl}_2$ ) solution, as illustrated by the following chemical equation.



The copper chloride solution is then mixed with sodium hydroxide ( $\text{NaOH}$ ) to form copper hydroxide,  $\text{Cu}(\text{OH})_2$ , and sodium chloride ( $\text{NaCl}$ ), as shown in the following reaction equation.



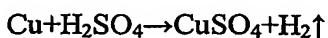
The copper hydroxide is precipitated and harvested; it is then converted by heating into copper oxide as shown in the following chemical equation.



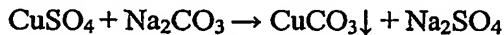
The sodium chloride is crystallized by heating before it is used as an industrial raw material. The copper oxide can be used directly as an industrial raw material. It must be noted here that the ionization of copper by the hydrochloric acid can be accelerated by use of hydrogen peroxide, aeration, or electrode.

It must be noted here that the hydrochloric acid may be replaced by an electroplating waste fluid, etching waste fluid, or copper chloride waste fluid, which is a waste product of the manufacturing process of PCB. These waste fluids contain copper, as well as ionizing acid capable of ionizing the copper. The copper ions are then reduced by sodium hydroxide (NaOH), thereby resulting in formation of copper carbonate (CuCO<sub>3</sub>), which is then converted by heating into copper oxide(CuO).

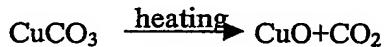
Referring to Fig. 3, a third method embodied in the present invention is designed to recycle copper from the discarded printed circuit boards. In the first place, the discarded printed circuit boards are immersed in the sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), thereby resulting in formation of copper sulphate (CuSO<sub>4</sub>) as shown in the following chemical equation.



A reducing agent, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), is added to the copper sulphate solution, thereby resulting in formation of copper carbonate (CuCO<sub>3</sub>) and sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) as shown in the following chemical reaction.



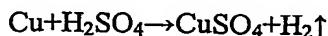
The copper carbonate is precipitated and harvested; it is then converted by heating into copper oxide (CuO), which is used as an industrial raw material.



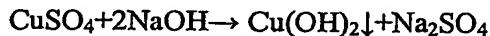
The ionization of copper by sulphuric acid can be enhanced by use of hydrogen peroxide, aeration, or electrode. The byproduct, such as sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), is crystallized by heating prior to being used as an industrial raw material.

It must be noted here that the hydrochloric acid may be replaced by an electroplating waste fluid, etching waste fluid, or copper chloride waste fluid, which is a waste product of the manufacturing process of PCB. These waste fluids contain copper, as well as ionizing acid capable of ionizing the copper. The copper ions are then reduced by sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), thereby resulting in formation of copper carbonate (CuCO<sub>3</sub>), which is then converted by heating into copper oxide (CuO).

As shown in Fig. 4, a fourth method embodied in the present invention is used to recycle copper contained in the PCB. The method involves a first step in which the discarded printed circuit boards are immersed in the sulphuric acid ( $H_2SO_4$ ), thereby resulting in formation of copper sulphate ( $CuSO_4$ ) as shown in the following chemical reaction.



A reductant, sodium hydroxide ( $NaOH$ ), is added to the copper sulphate ( $CuSO_4$ ) solution to form copper hydroxide,  $Cu(OH)_2$ , and sodium sulphate,  $Na_2SO_4$ , as shown in the following chemical equation.



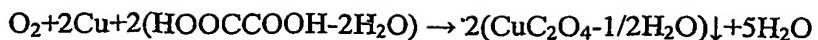
The copper hydroxide,  $Cu(OH)_2$ , is harvested and then converted by heating into copper oxide ( $CuO$ ) as shown in the following chemical reaction.



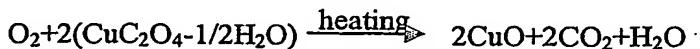
The ionization of copper by sulphuric acid ( $H_2SO_4$ ) may be accelerated by use of hydrogen peroxide, aeration, or electrode. The copper oxide so formed can be used directly as an industrial raw material, while the sodium sulphate ( $Na_2SO_4$ ) is crystallized by heating prior to being useful as industrial raw material.

It must be noted here that the hydrochloric acid may be replaced by an electroplating waste fluid, etching waste fluid, or copper chloride waste fluid, which is a waste product of the manufacturing process of PCB. These waste fluids contain copper, as well as ionizing acid capable of ionizing the copper. The copper ions are then reduced by sodium hydroxide ( $NaOH$ ), thereby resulting in formation of copper carbonate ( $CuCO_3$ ), which is then converted by heating into copper oxide ( $CuO$ ).

Referring to Fig.5, a fifth method embodied in the present invention is designed to recycle copper from the discarded printed circuit boards. The method involves an initial step in which the discarded printed circuit boards are immersed in a solution of oxalic acid ( $HOOCCOOH \cdot 1/2H_2O$ ). As a result, a powdered copper oxalate ( $CuC_2O_4 \cdot 1/2H_2O$ ) is formed, as shown in the following chemical equation.



The precipitate of copper oxalate is converted by heating in presence of oxygen into copper oxide (CuO), as shown in the following chemical equating.



It must be noted here that the precipitate of copper oxalate ( $\text{CuC}_2\text{O}_4 \cdot 1/2\text{H}_2\text{O}$ ) is obtained by filtration. The copper oxide so produced is directly used as an industrial raw material.

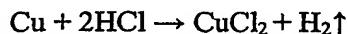
As shown in Fig.6, a device is designed for use in the methods of the present invention as described above with reference to Figs.1 through Fig.5. The device comprises a reaction tank 10, a precipitation bath 20, a conversion oven 30, and a heater 40. The reaction tank 10 is provided in the wall with an acid exit 11. The precipitation bath 20 is provided in the wall with an acid inlet 21, an outlet 22, and a discharge port 23 of sodium salt. The acid inlet 21 is connected with the acid exit 11 of the reaction tank 10 by a connection pipe 24 which is provided with a valve 241. The precipitation bath 20 is provided with an electric agitator M. The conversion oven 30 has a feeding port 31, a discharging port 32, a feeding controller 33, a see-through window 34, an isolation tank 35, and a dust remover 36. The feeding port 31 is located at the top of the conversion oven 30. The discharging port 32 is located at the bottom of the conversion oven 30. The feeding controller 33 is disposed under the feeding port 31 for controlling the feeding speed. The see-through window 34 is located in the wall of the conversion oven 30 to facilitate the visual observation of the process in progress. The isolation tank 35 is disposed on the discharging port 32 for preventing copper oxide (CuO) from being contaminated in the course of transfer of the copper oxide. The dust remover 36 comprises a dust collecting tube 361, a water bath 362, and a venture tube dust cleaner 363. The dust collecting tube 361 is connected to the wall of the conversion oven 30. The venture tube dust cleaner 363 is mounted on the tube wall of the dust collecting tube 361. A water pipe 364 is connected with the venture tube dust cleaner 363 and the water bath 362. The water pipe 364 is provided with a pump 365. The venture tube dust cleaner 363 has a suction force, by means of which the steam and the powdered copper oxide are drawn from the conversion oven 30 into the dust collecting tube 361. Meanwhile, the water

is pumped by the pump 365 into the venturi tube dust cleaner 363 from the water bath 362, so as to facilitate the collecting of the powdered copper oxide and the steam in the water bath 362 in which the copper oxide precipitates. The heater 40 is disposed in the interior of the conversion oven 30 and is provided with a plurality of conveyers 41 which are used to extend the reaction and to turn over the conversion product. Each set of conveyers 41 is provided with a heating apparatus 42 by which the temperature of the interior of the conversion oven 30 is kept between 230 and 350. In addition, the conveyers 41 are provided therebetween with a crushing wheel 43 and a dust shield 44 which is located over the crushing wheel 43 to avert dispersion of dust.

Now referring to Fig.1 and Fig.6, the operation of the device of the present invention calls for an introduction of an appropriate amount of hydrochloric acid (HCl) into the reaction tank 10. Subsequently, a predetermined number of the discarded printed circuit boards are immersed in the reaction tank 10 containing the hydrochloric acid (HCl). As a result, the copper of the discarded printed circuit boards is ionized to form a copper chloride solution, which is transferred via the valve 241 to the precipitation bath 20. As soon as the precipitation bath 20 contains an appropriate amount of the copper chloride solution, the valve 241 is shut off. An appropriate amount of sodium carbonate ( $Na_2CO_3$ ) is added to the precipitation bath 20. The mixture is stirred thoroughly by the electric agitator M. The reaction products, sodium chloride ( $NaCl$ ) and copper carbonate ( $CuCO_3$ ), are formed, with the sodium chloride ( $NaCl$ ) being discharged via the discharging port 23 of the precipitation bath 20. The sodium chloride is crystallized by heating and is then used as an industrial raw material. In the meantime, the copper carbonate ( $CuCO_3$ ) is precipitated at the bottom of the precipitation bath 20 and is discharged via the outlet 22 of the precipitation bath 20 such that the copper carbonate is put through a washing-dehydrating equipment "P", and that the copper carbonate is fed into the conversion oven 30 via the feeding port 31 of the conversion oven 30. The copper carbonate is heated in the interior of the conversion oven 30 in such a manner that it moves from one conveyer 41 to another. The copper carbonate ( $CuCO_3$ ) is thus converted by heating into copper oxide ( $CuO$ ), which is discharged via the discharging port 32 and is used as an industrial raw material.

As far as the embodiments described with reference to Fig.2 through Fig.5, the device is operated in similar manners described above with reference to Fig.1 and Fig.6.

Referring to Fig. 7, a sixth method embodied in the present invention is intended to recycle copper from the discarded printed circuit boards. The method comprises a first step in which a predetermined number of the discarded printed circuit boards are immersed in a hydrochloric acid solution for ionizing the copper contained in the discarded printed circuit boards, thereby resulting in formation of a copper chloride ( $CuCl_2$ ) solution as shown in the following chemical equation.

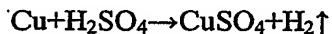


The copper chloride ( $CuCl_2$ ) solution is mixed with an aluminum material to form the copper powder and a poly aluminium chloride,  $[Al_2(OH)_nCl_{6-n} \cdot XH_2O]_m$ , aqueous solution, as shown in the following chemical reaction.

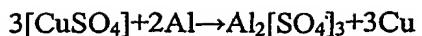


In the above chemical equation,  $n=1-5$ ,  $m \leq 10$ . The aluminum material is dissolved in the copper chloride solution. The aluminum material is recycled from the discarded material containing aluminum, or from the aluminium chips, so as to reduce the cost. In light of aluminium molecule being greater in activity than copper molecule, the copper of the copper chloride ( $CuCl_2$ ) is replaced by the aluminium, thereby resulting in production of copper powder. The aqueous solution of the poly aluminium chloride  $[Al_2(OH)_nCl_{6-n} \cdot XH_2O]_m$  is used as a metal PAC in the water treatment.

As shown in Fig.8, a seventh method embodied in the present invention is used to recycle copper from the discarded printed circuit boards. The method involves an initial step in which the discarded printed circuit boards are immersed in a sulphuric acid solution ( $H_2SO_4$ ), thereby resulting in formation of a copper sulphate ( $CuSO_4$ ) solution, as shown in the following chemical equation.



The copper sulphate solution is then mixed with an aluminium material to form copper powder and an aluminium sulphate aqueous solution ( $Al_2[SO_4]_3$ ), as shown in the following chemical reaction.



The aluminium material is obtained from the discarded material containing aluminium, or from the aluminium chips, so as to reduce the cost. In light of the aluminium molecule being greater in activity than the copper molecule, the copper of the copper sulphate ( $\text{CuSO}_4$ ) is replaced by the aluminium, thereby resulting in production of copper powder. The  $\text{Al}_2[\text{SO}_4]_3$  aqueous solution is used as a metal PAC in the water treatment.

Referring to Fig.9, a device is used to carry out the methods described above with reference to Fig.7 and Fig.8. The device comprises a reactor 50, an acid reservoir 60, a PAC reaction precipitation bath 70, a water tower 80, and a PAC washing and storing apparatus 90. The reactor 50 and the acid reservoir 60 are connected by a pipe 51 which is provided with a valve 52. The acid reservoir 60 is provided in the wall with a solution transporting pipe 61 which is in turn provided with a pump 62. The pipe 61 has one end, which is extended into the PAC reaction precipitation bath 70. Located at the top of PAC reaction precipitation bath 70 is a basket 71 for holding aluminium. Located at the bottom of the precipitation bath 70 is a copper powder exit 72. The precipitation bath 70 is further provided in the wall with a reaction circulation pipe 73, which is provided with a reaction circulation pump 74 and a reaction circulation valve 75. The reaction circulation pipe 73 has one end which is located at the top of the basket 71. A PAC drain pipe 76 is disposed on the reaction circulation pipe 73 located between the reaction circulation pump 74 and the reaction circulation valve 75. The PAC drain pipe 76 is provided with a PAC output valve 77. The end of the drain pipe 76 is extended into the PAC washing and storing apparatus 90. The water tower 80 is provided in the wall with a water pipe 81 which is provided with a reaction water admission valve 82 and has one end being extended into the reaction precipitation bath 70. The PAC washing and storing apparatus 90 has a washing and filtering tank 91 and a PAC storage tank 92. The washing and filtering tank 91 is provided at the top with a filter 93 and is provided in the wall with a PAC output pipe 94 which is provided with a pump 95. The top of the washing and filtering tank 91 is connected with a PAC filtration pipe 96, a PAC storage pipe 97 and a return pipe 98. The PAC filtration pipe 96, the PAC storage pipe 97, and the return pipe 98 are all connected with the PAC output pipe 94 and are provided with a valve "V". The filter 93 and the water tower 80 are connected by a washing pipe 931 which is provided with a valve 932.

Now referring to Fig.7 through Fig.9, the operation is carried out by providing the reactor 50 with an appropriate amount of hydrochloric acid (HCl) or sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Thereafter, a predetermined number of the discarded printed circuit boards are immersed in the reactor 50 for the purpose of effecting the ionization of copper contained in the discarded printed circuit boards, so as to form a solution containing copper. The valve 52 is then opened to allow the copper-containing solution to flow into the acid reservoir 60. As soon as the acid reservoir 60 contains an appropriate amount of the copper-containing solution, the valve 52 is shut off. An appropriate amount of an aluminium material is held in the basket 71. Meanwhile, the reaction water admission valve 82 is opened to allow a small amount of clean water to enter the reaction precipitation bath 70. The pump 62 is then started to pump the copper-containing solution into the PAC reaction precipitation bath 70 from the acid reservoir 60. The reaction circulation pump 74 is simultaneously started while the reaction circulation valve 75 is opened. As a result, the aluminium material held in the basket 71 is thoroughly bathed in the copper-containing solution until such time when the PAC reaction precipitation bath 70 is filled with the copper-containing solution. The copper of the copper-containing solution is replaced by aluminium. The aluminium product is precipitated at the bottom of the PAC reaction precipitation bath 70 and is then discharged via the copper powder exit 72. The PAC solution produced in the reaction is allowed to enter the washing and filtering tank 91 via the PAC output valve 77 and the drain pipe 76. The valve "V" of the PAC filtration pipe 96 is opened to allow the passage of the PAC solution through the filter 93. The valve "V" of the PAC storage pipe 97 is then opened to allow the clean PAC solution to enter the PAC storage tank 92. Upon completion of the filtration of the PAC solution, the valve 932 of the washing pipe 931 is opened to allow the water in the water tower 80 to wash the filter 93 via the washing pipe 931. The waste water contains PAC and is sent back to the PAC reaction precipitation bath 70 via the return pipe 98.

The copper-recycling methods of the present invention produce no by-product hazardous to environment. The present invention described above is to be regarded in all respects as being illustrative and nonrestrictive. Accordingly, the present invention may be embodied in other specific forms without deviation from the spirit thereof. The present invention is therefore to be limited only by the scopes of the following claims.